**Standard Operating Procedure for the Determination of Organic Compounds in Drinking Water By Liquid-Solid Extraction and Capillary Column Gas Chromatography Mass Spectrometry**

1. Scope and Application

1.1 This method is applicable for the determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a $C_{18}$ organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatography.

| Analyte | CAS # | Analyte | CAS # |
|---|---|---|---|
| Aldrin | 309-00-2 | Alachlor | 15972-60-8 |
| Atrazine | 1912-2429 | Butachlor | 23184-66-9 |
| BHC-alpha | 319-84-6 | BHC-beta | 319-85-7 |
| BHC-delta | 319-86-8 | BHC-gamma (Lindane) | 58-89-9 |
| Chlordane-alpha | 5103-71-9 | Chlordane-gamma | 5103-74-2 |
| Chlorothalonil | 1897-45-6 | Chlorpyrifos | 2921-88-2 |
| Cyanazine | 21725-46-2 | 4,4'-DDD | 72-54-8 |
| 4,4'-DDE | 72-55-9 | 4,4'-DDT | 50-29-3 |
| Diazinon | 333-41-5 | Dieldrin | 60-57-1 |
| DCPA | 709-98-8 | Endosulfan I | 959-98-8 |
| Endosulfan II | 33213-65-9 | Endosulfan Sulfate | 1031-07-8 |
| Endrin | 72-20-8 | Endrin Aldehyde | 7421-93-4 |
| Endrin Ketone | 53494-70-5 | Ethalfluralin (Sonolan) | 55283-68-6 |
| Fenvalerate | 51630-58-1 | Heptachlor | 76-44-8 |
| Heptachlor Epoxide | 1024-57-3 | Hexachlorobenzene | 118-74-1 |
| Hexachlorcyclopentadiene | 77-47-4 | Malathion | 121-75-5 |
| Metolachlor | 51218-45-2 | Methoxychlor | 72-43-5 |
| Metribuzine | 21087-64-9 | Mirex | 2385-85-5 |
| Parathion Ethyl | 56-38-2 | Parathion Methyl | 298-00-0 |
| Propachlor | 1918-16-7 | Propiconazole (Tilt) | 60207-90-1 |
| Pendimethalin | 40487-42-1 | Simazine | 122-34-9 |
| trans-Nonachlor | 39765-80-5 | Triallate (Far-Go) | 2303-17-5 |
| Trifluralin (Treflan) | 1582-09-8 | | |

| Multi-Component Analytes | CAS # |
|---|---|
| Arochlor 1016 | 12674-11-2 |
| Arochlor 1221 | 11104-28-2 |
| Arochlor 1232 | 11141-16-5 |
| Arochlor 1242 | 53469-21-9 |
| Arochlor 1248 | 12672-29-6 |
| Arochlor 1254 | 11097-69-1 |

| | |
|---|---|
| Arochlor 1260 | 11096-82-5 |
| Chlordane (Tech.) | |
| Toxaphene | 8001-35-2 |

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero (1). The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. The concentration calibration range demonstrated in this method is 0.1ug/L to 10ug/L for most analytes.

2. Summary of Method

2.1 Organic compound analytes, internal standards and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge (J.T. Baker, Speedisk, p/n 8063-06) or disk (3M Empore, Fisher p/n 14-386-2) containing a solid matrix with a chemically bonded $C_{18}$ organic phase. This extraction is performed on a Horizon SPE-Dex 4770 Extractor. The organic compounds are eluted from the liquid-solid extraction (LSE) cartridge or disk with small quantities of ethyl acetate followed by methylene chloride. Sample is concentrated down to 1 mL via Zymarks. The sample components are separated, identified and quantitated by injecting an aliquot of the concentrated extract into a gas chromatography / mass spectrometer (GC/MS).

3. Definitions

3.1 INTERNAL STANDARD (IS): A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The IS must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SURR): A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (DUP): Two sample aliquots taken in the analytical lab and analyzed separately with identical procedures. Analysis should give a measure of the precision associated with laboratory procedures, but not with collection, preservation or storage procedures.

3.4 LABORATORY REAGENT BLANK (LRB): An aliquot of reagent water that is

treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC): A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined method criteria.

3.6 LABORATORY FORTIFIED BLANK (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the lab is capable of making accurate and precise measurements at the required method detection limit.

3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the lab. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 STOCK STANDARD SOLUTION: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the lab with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.9 PRIMARY DILUTION STANDARD SOLUTION: A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration and other analyte solutions.

3.10 CALIBRATION STANDARDS (CAL): A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.11 QUALITY CONTROL SAMPLE (QCS): A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the lab, and is used to check laboratory performance with externally prepared test materials.

4. Interferences

4.1 During analysis, major contaminant sources are reagents an liquid-solid extraction devices. Analyses fo field and laboratory reagent blanks provide information about the presence of contaminants.

4.1.1 Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent or soaking in detergent water and washing afterwards. Thoroughly rinse with tap and reagent water and let drain dry. Rinse glassware with acetone first, followed by hexane and let drain dry.

4.1.2 After drying, store glassware in a clean environment. To prevent any accumulation of dust or other contaminants, store inverted or capped with aluminum foil.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe with an appropriate solvent can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of solvent can be made to ensure that accurate values are obtained for the next sample.

4.5 It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used for sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected. Also, the use of high purity solvents and reagents will minimize interferences.

5. Safety

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method.

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standards solutions of these compounds should be handled with suitable protection to skin,

eyes, etc.

6.0 Equipment and Supplies

NOTE: Brand names, suppliers and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 pH paper or pH meter

6.2 Glassware, ALL glassware must be meticulously cleaned with detergent water, rinsed with DI water followed by solvent rinsing (acetone and hexane).

6.3 Field sample containers. 4-L or 1 gallon amber glass bottles fitted with Teflon-lined screw caps.

6.4 Lab sample containers. 1-L or 1 quart amber glass bottles fitted with Teflon-lined screw caps.

6.5 Volumetric flasks, various volumes.

6.6 Eppendorf auto-pipetters or volumetric/graduated pipets of various volumes

6.7 Micro syringes, various sizes.

6.8 Vials. Various sizes of amber vials with Teflon-lined screw caps.

6.9 Drying columns. The drying tube should contain 5-7 grams of anhydrous sodium sulfate to prohibit residual water from contaminating the extract.

6.10 Analytical balance capable of weighing to 0.0001 grams accurately.

6.11 Horizon SPE-DEX 4770 Extractor.

6.12 Vacuum System to maintain a minimum vacuum of approximately 25 inches of mercury.

6.11 200 ml Zymark concentration tubes.

6.12 Zymark Turbo-Vap concentrator/evaporator

6.13 Nitrogen gas supply with gas flow controller

6.14 Gas Chromatography Columns: Any capillary column that provides adequate resolution, capacity, accuracy and precision. Medium polar, low bleed columns are recommended. The following phases are suitable for pesticide analysis, but this list is not all inclusive of the phases or columns that may be used. Column length and diameters used in this lab are 30 or 60 meters in length and 0.25 microns in diameter from J&W (DB-5MS).

6.15 Gas chromatograph / mass spectrometer / data system (GC/MS/DS).

6.15.1 The GC must be capable of temperature programming and be equipped for splitless/split injection.

6.15.2 The MS must be capable of electron ionization at a normal electron energy of 70 eV to produce positive ions. The MS must be capable of scanning at a minimum from 45 to 450 amu with a complete cscan cycle time of 1 second or less. The MS must meet DFTPP criteria for an approximately 5 ng DFTPP sample.

6.15.3 The interfaced data system is required to acquire, store, reduce and output MS data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given RT window, comparing the mass spectrum's RT and quant ions of interest with some sort of library.

7. Reagents and Standards

7.1 Helium carrier gas, as contaminant free as possible.

7.2 Liquid-solid extraction cartridges for Horizons. Disks or cartridges need to be inert such that phthalates and adipates do not leach into ethyl acetate and methylene chloride eluent. The disks or cartridges are composed of a $C_{18}$ surface and have diameter of 47 mm. The disks used in this lab are from Fisher (3M Empore High Performance Extraction Disks, p/n 2215) and the cartridges used are from J.T. Baker ( Bakerbond Speedisk, $C_{18}$XF, p/n 8063-06)

7.3 Solvents

7.3.1 Methylene chloride, ethyl acetate, MTBE and methanol. High purity pesticide quality or equivalent.

7.3.2 Nano Water.

7.4 Hydrochloric acid, 6N

7.5 Sodium sulfate, anhydrous.

7.6 The following mixture is to be used as the internal standard: Acenaphthalene-d10, Chrysene-d12 and Phenanthrene-d10. Purchased from Crescent Chemical Company (500ug/mL), Catalog #CC2494.

7.7 The following mixture is to be used as the surrogate standard: 1,3-Dimethyl-2-nitrobenzene, Perylene-d12 and Triphenylphosphate. Purchased from Crescent Chemical Company (500ug/mL), Catolog #CC2495.

7.8 4-Terphenyl-d14 - fortification solution. Purchased from Crescent Chemical Company (500ug/mL), Catalog #CC2079A

7.9 Mirex - alternate surrogate standard. Purchased from Crescent Chemical Company (100ug/mL), Catalog #7795M.

7.10 Stock Standard Solution - For drink water samples a stock standard solution is purchased from Crescent Chemical Company (100 ug/mL), Catolog #CCS376. For ground water samples, three customized standard solutions are purchased from Protocol Analytical Supplies Inc. (100ug/mL), Catolog #NDDH-ISA-13, NDDH-ISB-13 and NDDH-ISC-12.

7.10.1 Prepare three 5 ug/mL intermediate stock standard solution of the three Protocol customized standards by accurately pipetting the appropriate amount of stock standard into a desired volumetric flask and bring up to volume with methanol (or suitable solvent). Methylene chloride should be avoided as a solvent for standards because of its high vapor pressure leads to rapid evaporation and concentration changes. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.10.2 Store stock standard solutions in glass vials, clear or amber, with TFE-fluorocarbon-sealed screw tops. Store solutions at appropriate temperatures, such as room (ambient) or 4° C.

7.10.3 Replace Stock Standard Solutions when a problem is indicated.

7.13 Internal Standard Stock Solution - Prepare 100ug/mL intermediate internal

standard solutions by accurately pipetting the appropriate amount of stock standard into a desired volumetric flask and bring up to volume with methanol (or suitable solvent). Store solution in a TFE-fluorocarbon-sealed screw cap bottle and store at appropriate temperature.

7.14 Surrogate Standard Stock Solution - Either CCS-2495 mixture or Mirex. can be used. The surrogate can be prepared in lab or be commercially prepared, in our case, they are purchased from Crescent Chemical Company at a concentration of 500ug/mL and 100ug/mL respectively.

7.15 GC /MS performance check solution - The following solution can also be purchased as a commercially prepared check solution. Prepare a 5 ug/mL solution containing Endrin, 4,4'-DDT and DFTPP in methylene chloride. This solution will be injected to check for undesirable degradation of these compounds in the injection port by looking for endrin aldehyde and endrin ketone or for 4,4'-DDE and 4,4'-DDD.

7.16 Calibration solutions (CAL1 through CAL6). Prepare a series of six concentration calibration solutions in methylene chloride which contain analytes fo interest (except pentachlorophenol, toxaphene and the Aroclor compounds) at suggested concentrations of 0.1, 0.5, 1, 2, 5 and 10 ug/mL, with a concentration in the range of 2-5 ug/mL of each internal standard and surrogate in each CAL solution. Samples containing toxaphene and Aroclor compounds are analyzed on a GC-ECD instrument.

8. Sample Collection, Preservation, and Storage

8.1 Sample collection. When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2 minutes). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

8.2 Sample dechlorination and preservation. All samples should be iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of a reducing agent. Add 40-50 mg of sodium sulfite to each liter of water.

8.2.1 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in stored sample. Cyanazine must to be dechlorinated and acidified just prior to extraction. They should be analyzed within 14 days of collection.

8.2.2 Atraton and prometon are not efficiently extracted from water at pH 2 due to what appears to be their ionization in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no acid should be added. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%.

8.3 Holding time. Results of the time/storage study of all method analytes showed that all but six compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved and stored as described in Section 8.2. Therefore, samples must be extracted within 14 days from the time of collection. Samples being analyzed for: Carboxin, diazinon, disulfoton, disulfoton sulfoxide, fenamiphos, and terbufos must be extracted immediately after collection and preservation. Sample extracts may be stored at $4^0$ C for up to 30 days after extraction.

8.4 Field blanks.

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with the filled sample bottles.

8.4.2 When sodium sulfite and Hydrochloric acid are added to the samples, use the same procedure to add the same amounts to the FRB.

8.5 Extracts are stored at 4° C and away from light. A 14 day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. Quality Control

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of LRB, LFB, and LFM. A MDL should be determined for each analyte of interest. The laboratory must maintain records to document the quality of the data generated.

9.2 Initial demonstration of low back ground for each new supply of the extraction disk or cartridge from the supplier needs to show that a LRB is reasonably free of contamination that would prevent the determination of any analyte of concern. This experiment must also that the particle size and packing for the LSE cartridges or disks are acceptable. This is determined by obtaining a consistent flow rate with all samples.

9.2.1 A source of potential contamination is the LSE cartridge or disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.2 Other sources fo background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background form method analytes should be below the MDL.

9.2.3 One liter of water should pass through a cartridge in about 2 hours with a partial vacuum of about 13 cm (5 in.) of mercury. Typically for the Horizon it is approximately 20 minutes when using either the cartridge or disk.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a LFB containing each analyte of concern at a suggested concentration in the middle of the calibration curve (2-5 ug/mL). This will be dependent on the sensitivity of the instrumentation used.

9.3.1 Prepare each replicate by adding sodium sulfite and 6N HCl according to Section 8.2, then adding the appropriate aliquot of intermediate standard, or certified quality control sample, to reagent water. Analyze each replicate accordingly.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the

mean concentration of each analyte in all replicates and the mean accuracy (as mean percentage of true value, T.V.) For each analyte, and the precision (as RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as percentage of the T.V., should be 70-130% and the RSD should be <30%. If these criteria are not met, locate the source of the problem, and repeat with freshly prepared LFBs.

9.3.4 Analyze seven replicate LFBs which have been fortified with all analytes of interest at approximately 0.5 ug/L. Calculate the MDL of each analyte using the procedure described in Section 13.1.2 (1). It is recommended that these analyses be performed over a period of three to four days to produce more realistic method detection limits.

9.3..5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Section 10.3). In LFBs or samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in LFBs and samples. The addition of 10uL of the recovery standard, terphenyl-d14 (500ug/mL), to the extract si recommended to be used to monitor the recovery of the I.S. in LFBs and samples. Internal standards recovery should be > 70%.

9.5 With each batch of samples processed as a group within a 12 hour shift, analyze a LRB to determine the background system contamination. Any time a new shipment of LSE disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Section 9.2.

9.6 With each batch of samples processed as a group with a work shift, analyze a single LFB containing each analyte of concern at a concentration as determined in Section 9.3. If more than 20 samples are extracted in a batch, analyze a LFB for every 20 samples. LFB for each analyte should fall within 70-130% as described in Section 9.3.3. If any analyte fall outside of 70-130%, the problem for that particular analyte must be located and corrected before additonal samples are analyzed. Add the results to the on-going control charts to document data quality.

NOTE: If a sample is to be analyzed for PCB and/or toxaphene, a separate LFB must be made.

9.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of LFM samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with LFBs. If a variety of different sample matrices are analyzed regularly, such as drinking water from groundwater and surface water sources, matrix independence should be established for each. Like LFBs, LFMs should be analyzed for every 20 samples processed in the same batch. If the recovery data for a LFM does not meet the 70-130% criteria and LFBs show the laboratory to be in control, then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.8 With each set of samples, a field reagent blank (FRB) should be analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.

9.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Section 9.3.3), check the entire analytical procedure. To locate and correct the problem source.

9.10 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. Calibration and Standardization

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required each day or at the beginning of each period in which analyses are performed not to exceed 12 hours. It is recommended that an additional calibration check be performed at the end of each period of continuous instrument operation, so that all field sample analyses are bracketed by a calibration check standard.

10.2 Initial calibration

10.2.1 Calibrate the mass and abundance scales of the MS with the calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.2.2.

10.2.2 Inject a 5ug/mL solution of DFTPP, Endrin and DDT. Acquire a mass spectrum that includes data for m/z 45-450. If the DFTPP mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. Locate any degradation products of endrin ( endrin ketone, [EK] and endrin aldehyde [EA]) and DDT (DDE and DDD) at their appropriate RTs and quantitation ions. If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with calibration. Calculate percent breakdown using peak areas based on total ion current (TIC) as follows:

% DDT breakdown =

$$\frac{\text{TIC area of DDT degradation peaks (DDE+DDD)}}{\text{TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% Endrin breakdown=

$$\frac{\text{TIC area of Endrin degradation peaks (EA+EK)}}{\text{TIC area of total Endrin peaks (Endrin+EA+EK)}} \times 100$$

10.2.3 Inject a medium concentration (0.5-2ug/mL) calibration solution, in our case, usually large volume (1-10uL), and acquire and store data from m/z 45-450 with an appropriate total cycle time. Calibration standards for toxaphene and Aroclors need to be analyzed on GC-ECD instrumentation.

10.2.3.1 The ramping program needs to be able to separate the analytes of interest such that it each analyte can be characterized, therefore, one can use either a multi-ramp temperature program or single ramp linear program.

10.2.4 Performance criteria for the calibration standards. Examine the stored GC/MS data with the data system software.

10.2.4.1 GC performance. Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the aver peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC coolumn requires maintenance. See Section 10.3.6.

10.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a peak in the appropriate RT window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Section 10.3.3.6.

10.2.5 If all performance criteria are met, inject same volume of aliquot (1-10uL) of each of the other CAL solutions using the same GC/MS conditions.

10.2.5.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. In this case, the analyst should prepare additional CAL solutions at slightly higher concentrations to obtain at least 5 calibration points that bracket the expected analyte concentration range.

10.2.6 Calculate a response factor (RF) for each analyte of interest and surrogate for each CAL solution using the internal standard whose RT is nearest the RT of the analyte or surrogate. In our case, the GC/MS data system software generates a RF for each analyte from a calibration curve.

10.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 12 hour work shift during which analyses are performed using the following procedure.

10.3.1 Inject an aliquot (1-10uL) of 5ug/mL solution of DFTPP, endrin and DDT. Acquire a mass spectrum for the DFTPP that includes data for m/z 45-450. Ensure that all criteria in Section 10.2.2 are met.

10.3.2 Inject an aliquot (1-10uL) of a calibration solution and analyze with the same conditions used during the initial calibration. It is recommended that the concentration of the calibration solution be varied, so that the calibration can be verified at more than one point.

NOTE: If the continuing calibration check standard contains the PCB congeners listed in Section 1, calibration verification is not required for each Aroclor. Calibration verification of toxaphene should be performed at least once each 24 hour period.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not changed by more than 30% form the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. Control charts are useful aids in documenting system sen These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration. sensitivity changes.

10.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. If a linear regression is used, the calculated amount for each analyte must be within 30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. Any field sample extracts that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored.

10.3.5.1 Because of the large number of compounds on the analyte list, it is possible fro a few analytes of interest to be outside the continuing calibration criteria. If analytes the missed the calibration check are detected in samples, they may be quantified using a single point calibration. The single point standards should be prepared at a concentrations that produce responses close (within 20%) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action MUST be taken. If 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action MUST be taken.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

10.3.6.3 Flush the GC column with solvent according to manufacturer's

instruction manul.

10.3.6.4 Break off a short portion (approximately 1 meter) of the column from the end near the injector; or replace GC column. Ths action will cause a change in retention times.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean MS ion source and rods (if a quadrupole).

10.3.6.7 Replace filaments.

10.3.6.8 Replace any components that allow analytes to come in contact with hot metal surfaces.

10.3.6.9 Replace the MS electron multiplier, or any other faulty components.

11 Procedure

11.1 Sample preparation (Pre-extraction)

11.1.1 Mark meniscus of water level in sample container (for later measurement) if 1 liter bottle is used. If 4 liter bottle is used, measure 1 liter into a 2 liter separatory funnel. Add 1 liter of reagent water to appropriate separatory funnels for blanks and blank spikes.

11.1.2 Adjust pH to approximately 2 by adding 2 ml of 6N HCL. Measure pH with indicator paper or pH meter.

11.1.3 Add 10 mL of methanol, seal and shake to mix.

11.1.4 Add surrogate spike to each sample, add matrix spike and blank spike to each appropriate sample (Table 5 of EPA Method 525.2, page 525.2-44).

11.2 Horizon extractor prep

11.2.1 Make sure that the solvent bottles are full and that the waste containers are empty.

11.2.2 Turn on Nitrogen gas at the tank.

11.2.3 Turn on the vacuum supply.

11.2.4 Turn on the Horizon controller.

11.2.5 Select the method to be run on the controller by pressing buttons in the following order:

11.2.5.1 Press “Select” this allows for the selection an individual extractor or all extractors

11.2.5.2 Press “.” this allows for the selection of all extractors.

11.2.5.3 Press “Method” this allows for an extraction method to be chosen.

11.2.5.4 Press “525.9" this is the method to purge the extractors and allows for all solvents to be used. This allows the user to determine if the extractors are working properly before doing actual samples. If extractors are working properly continue, otherwise get extractors working.

11.2.5.5 Place the extraction disks into the extractors. Place collection vials in proper position.

11.2.5.6 Press “Select” followed by “.” followed by “Method” followed by “525.2". This allows for the proper method to be entered into the extractors. This method dispenses solvents and operates in the following order:

| | | |
|---|---|---|
| 11.2.5.6.1 | Prewet solvent 1 | Ethyl acetate |
| | Soak time | 1.5 min |
| | Dry time | 1.5 min |
| 11.2.5.6.2 | Prewet solvent 2 | Dichloromethane |
| | Soak time | 1.5 min |
| | Dry time | 1.5 min |
| 11.2.5.6.3 | Prewet solvent 3 | Methanol |
| | Soak time | 2 min |
| | Dry time | 0 min |
| 11.2.5.6.4 | Prewet solvent 4 | Water |

| | | |
|---|---|---|
| | Soak time | 2 min |
| | Dry time | 0 min |
| 11.2.5.6.5 | Sample addition | |
| | Dry time | 8 min |
| 11.2.5.6.6 | Rinse solvent 1 | Ethyl acetate |
| | Soak time | 2 min |
| | Dry time | 1 min |
| 11.2.5.6.7 | Rinse solvent | Ethyl acetate |
| | Soak time | 2 min |
| | Dry time | 1 min |
| 11.2.5.6.8 | Rinse solvent | Dichloromethane |
| | Soak time | 2 min |
| | Dry time | 1 min |
| 11.2.5.6.9 | Rinse solvent | Dichloromethane |
| | Soak time | 2 min |
| | Dry time | 1 min |
| 11.2.5.6.10 | Rinse solvent | Dichloromethane |
| | Soak time | 2 min |
| | Dry time | 5 min |

11.2.5.7 Press “Start” on each controller and Sect. 11.2.5.6 will begin.

11.2.5.8 After extraction is completed, the collected eluant needs to be dried. To dry the eluant add an appropriate amount of sodium sulfate (anhydrous) to the collection vial.

11.2.5.9 Prepare a drying column by placing a filter paper into a disposable drying column. Add about 3-4 inched of sodium sulfate to the column. Rinse the sodium sulfate with dichloromethane. Discard the dichloromethane. Place a Zymark collection tube under the prepared drying column. Add the eluant to the column collecting all. Rinse the collection vial from the Horizon with dichloromethane and add to the drying column. Rinse the drying column with dichloromethane. The sample is ready for concentration.

11.3 Extract Concentration

11.3.1 Concentrate the methylene chloride extract to approximately 1 to 3 ml in a Zymark Turbo Vap or round bottom flask for Rotovap. Exchange the solvents by adding approximately 10 ml of MTBE or hexane. Concentrate solvent to approximately 1 to 3 ml. Exchange the solvents once more by adding approximately 10 ml of MTBE or hexane. Concentrate solvent to approximately 1 to 3 ml.

11.3.2 Transfer contents to a graduated tube using disposable pipets, rinsing vessel (Zymark or round bottom flask) with MTBE or hexane and combining liquids.

11.3.3 Evaporate to 1 ml using block evaporator and nitrogen gas, exchanging twice more using MTBE or hexane.

11.3.4 Bring final volume to 1 ml in graduated tube.

11.3.5 Transfer contents to auto-sampler vial in preparation for GC/MS analysis.

11.4 Gas Chromatography

11.4.1 Follow the manufacturers "Operating Manual" for proper set-up and operation of the GC instrument being used. Optimize conditions of the GC system for analytes in question.

11.4.2 Calibrate the system before each set of samples using a minimum of 3 standards or use one standard to verify system calibration. The standards and extracts must be in the same solvent, whether it be MTBE or hexane.

11.4.3 If the internal standard calibration procedure is used, add the appropriate amount of internal standard to each extract prior to injection.

11.4.4 Record resulting peak size in area units.

11.4.5 If the response of the peak exceeds the working range of the system, dilute the extract and re-analyze on instrument. If internal standard calibration was used, add an appropriate amount of additional internal standard to maintain proper concentration.

11.4.6 Refer to the instrument manuals or other manufacturer's manuals on

specific details for trouble-shooting of the gas chromatograph and/or data system when problems arise.

11.5 Identification of Analytes

11.5.1 Identify a sample component by comparison of its retention time to the retention time of components in a standard reference chromatogram. If retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.5.2 Analytes identified by retention time, must fall within a retention time window. The width of window will vary from analyte to analyte based on the interpretation of the standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5.4 Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatogram. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor.

11.5.5 Analytes that are detected must be confirmed by the quantitative and qualitative peaks of the Scan spectra on the Mass Spectrometer.

12. Data Analysis and Calculations

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 2 of EPA Method 525.2, page 525.2-32. If the response of any analyte exceeds the calibration range established in Section 10, dilute the extract and re-analyze.

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Section 10. Do not use daily calibration verification data to quantitate analytes in samples.

$$Cx = \frac{(Ax)(Qis)}{(Ais)(RF)(V)}$$

where:

Cx – concentration of analyte or surrogate in ug/L in the water sample.

Ax – integrated abundance of the quantitation ion of the analyte in the sample.

Ais – integrated abundance of the quantitation ion of the internal standard in the sample.

Qis – total quantity (in micrograms) of internal standard added to the water sample.

V – original water sample volume in liters.

RF – mean response factor of analyte from the initial calibration. RF is a unitless value.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression established in Section 10. Do not use daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 ug/L, two significant figures for concentrations between 1-99 ug/L, and one significant figure for lower concentrations.

13. Method Performance

13.1 Single laboratory accuracy and precision data (Tables 3-6 of EPA Method 525.2, pages 525.2-36 through 525.2-2-51) for each listed analyte (except multi-component analytes) were obtained at a concentration 0.2 ug/L in reagent water utilizing the Horizon extraction procedure, and the HP GC/MS system.

13.1.1 With these data, the method detection limits (MDL) in the tables were calculated using the formula:

MDL = S t(n-1,1-alpha = 0.99)

where:

t(n-1,1-alpha = 0.99) = Student's t value for the 99% confidence level with n-1 degrees of freedom.

n = number of replicates

S = standard deviation of replicate analyses.

13.2 Problem compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used n this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photo degradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the disk was air dried longer than 10 min (Sect. 11) Drying times longer than 10 min should be avoided or nitrogen may be used to dry the disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 ug/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 ug/L level is not recommended because the concentration of the background in the blank is highly variable.

13.2.3 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. This suggests that metribuzin may break through C18 phase in highly contaminates samples resulting in low recoveries.

14. Pollution Prevention

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC 20036.

15 Waste Management

15.1 It is the laboratory's responsible to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, we "The Waste Management Manual for Laboratory Personnel", also available from the American Chemical Society at the address in Section. 14.

## 16 References

1. Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave, and W. L. Budde, "Trace Analysis for Wastewaters", Environ. Sci. Technol. 1981 15, 1426-1435, or 40 CFR, Part 136, Appendix B.

2. "Carcinogens - Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

3. "OSHA Safety and Health Standards, General Industry", (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Junk, G. A., M. J. Avery, J. J. Richard, "Interferences in Solid-Phase Extraction Using C18 Bonded Porous Silica Cartridges", Anal. Chem. 1988, 60, 1347.

**TABLE 1.** Ion Abundance Criteria For Bis(Perfluorophenyl)Phenyl Phosphine (DecaFluorotriphenylPhosphine, DFTPP)

| Mass (M/z) | Relative Abundance Criteria | Purpose of Checkpoint[1] |
|---|---|---|
| 51 | 10 - 80% of the base peak | low mass sensitivity |
| 68 | < 2% of mass 69 | low mass resolution |
| 70 | < 2% of mass 69 | low mass resolution |
| 127 | 10 - 80% of the base peak | low-mid mass sensitivity |
| 197 | < 2% of mass 198 | mid-mass resolution |
| 198 | base peak or > 50% of 442 | mid-mass resolution and sensitivity |
| 199 | 5 - 9% of mass 198 | mid-mass resolution and isotope ratio |
| 275 | 10 - 60% of the base peak | mid-high mass sensitivity |
| 365 | > 1% of the base peak | baseline threshold |
| 441 | Present and < mass 443 | high mass resolution |
| 442 | base peak or > 50% of 198 | high mass resolution and sensitivity |
| 443 | 15 - 24% of mass 442 | high mass resolution and isotope ratio |

[1]All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed t encourage some standardization to fragment patterns.

**TABLE 2** MDL calculations of LFB analytes.
True Value for each analyte is 0.20 ug/mL

| Date | Alachlor | Aldrin | Atrazine | BHC-alpha | BHC-beta | BHC-delta | BHC-gamma (Lindane) | Chlordane-alpha | Chlordane-gamma | Chlorothalonil | Chlorpyrifos |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/23/2002 | 0.23 | 0.14 | 0.29 | 0.18 | 0.26 | 0.23 | 0.20 | 0.20 | 0.21 | 0.24 | 0.21 |
| 6/3/2002 | 0.36 | 0.18 | 0.42 | 0.25 | 0.38 | 0.33 | 0.25 | 0.28 | 0.29 | 0.34 | 0.29 |
| 6/4/2002 | 0.24 | 0.10 | 0.29 | 0.21 | 0.25 | 0.22 | 0.24 | 0.18 | 0.19 | 0.23 | 0.20 |
| 6/18/2002 | 0.26 | 0.10 | 0.29 | 0.19 | 0.25 | 0.22 | 0.19 | 0.20 | 0.19 | 0.25 | 0.24 |
| 6/21/2002 | 0.21 | 0.16 | 0.26 | 0.19 | 0.23 | 0.21 | 0.19 | 0.19 | 0.2 | 0.23 | 0.18 |
| 6/24/2002 | 0.25 | 0.11 | 0.26 | 0.20 | 0.25 | 0.22 | 0.20 | 0.14 | 0.14 | 0.22 | 0.20 |
| 7/2/2002 | 0.23 | 0.15 | 0.28 | 0.18 | 0.25 | 0.23 | 0.21 | 0.19 | 0.19 | 0.23 | 0.21 |
| 7/15/2002 | 0.31 | 0.15 | 0.30 | 0.23 | 0.24 | 0.23 | 0.23 | 0.23 | 0.22 | 0.26 | 0.25 |
| 7/18/2002 | 0.22 | 0.10 | 0.21 | 0.15 | 0.15 | 0.14 | 0.14 | 0.14 | 0.14 | 0.16 | 0.18 |
| 7/23/2002 | 0.25 | 0.16 | 0.26 | 0.19 | 0.26 | 0.24 | 0.22 | 0.22 | 0.22 | 0.26 | 0.23 |
| 7/26/2002 | 0.15 | 0.12 | 0.18 | 0.14 | 0.16 | 0.16 | 0.15 | 0.17 | 0.17 | 0.16 | 0.15 |
| 7/29/2002 | 0.25 | 0.16 | 0.24 | 0.22 | 0.25 | 0.24 | 0.23 | 0.24 | 0.227 | 0.26 | 0.24 |
| 8/6/2002 | 0.26 | 0.14 | 0.25 | 0.17 | 0.20 | 0.20 | 0.18 | 0.19 | 0.19 | 0.25 | 0.21 |
| 8/13/2002 | 0.24 | 0.17 | 0.26 | 0.20 | 0.25 | 0.21 | 0.19 | 0.21 | 0.2 | 0.68 | 0.18 |
| 8/16/2002 | 0.31 | 0.24 | 0.32 | 0.26 | 0.26 | 0.32 | 0.25 | 0.26 | 0.26 | 0.33 | 0.29 |
| 9/6/2002 | 0.26 | 0.14 | 0.25 | 0.18 | 0.20 | 0.24 | 0.18 | 0.18 | 0.18 | 0.26 | 0.21 |
| 9/17/2002 | 0.30 | 0.15 | 0.31 | 0.23 | 0.26 | 0.25 | 0.24 | 0.22 | 0.22 | 0.26 | 0.22 |
| 9/17/2002 | 0.30 | 0.15 | 0.31 | 0.23 | 0.26 | 0.25 | 0.24 | 0.22 | 0.22 | 0.26 | 0.22 |
| 9/18/2002 | 0.29 | 0.20 | 0.29 | 0.26 | 0.26 | 0.25 | 0.26 | 0.26 | 0.25 | 0.25 | 0.25 |
| 9/24/2002 | 0.15 | 0.17 | 0.19 | 0.16 | 0.16 | 0.14 | 0.18 | 0.14 | 0.22 | 0.15 | 0.15 |
| 9/25/2002 | 0.29 | 0.18 | 0.37 | 0.29 | 0.26 | 0.26 | 0.31 | 0.22 | 0.21 | 0.36 | 0.26 |
| 10/29/2002 | 0.27 | 0.16 | 0.33 | 0.20 | 0.23 | 0.22 | 0.21 | 0.21 | 0.2 | 0.25 | 0.25 |
| 11/4/2002 | 0.17 | 0.07 | 0.14 | 0.14 | 0.16 | 0.16 | 0.15 | 0.13 | 0.12 | 0.17 | 0.16 |
| **Std Dev** | 0.051 | 0.037 | 0.061 | 0.040 | 0.049 | 0.047 | 0.040 | 0.040 | 0.038 | 0.105 | 0.039 |
| **MDL** | 0.129 | 0.093 | 0.153 | 0.100 | 0.123 | 0.117 | 0.101 | 0.100 | 0.096 | 0.263 | 0.099 |

**TABLE 2** MDL calculations of LFB analytes.
True Value for each analyte is 0.20 ug/mL

| Date | DDD | DDE | DDT | Diazinon | Dieldrin | Endosulfan I | Endosulfan II | Endosulfan Sulfate | Endrin | Endrin Aldehyde | Endrin Ketone |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/23/2002 | 0.29 | 0.21 | 0.25 | 0.22 | 0.22 | 0.20 | 0.25 | 0.24 | 0.26 | 0.24 | 0.31 |
| 6/3/2002 | 0.37 | 0.32 | 0.36 | 0.28 | 0.32 | 0.28 | 0.31 | 0 | 0.36 | 0.3 | 0.40 |
| 6/4/2002 | 0.23 | 0.19 | 0.23 | 0.18 | 0.20 | 0.20 | 0.24 | 0.22 | 0.23 | 0.25 | 0.26 |
| 6/18/2002 | 0.29 | 0.2 | 0.26 | 0.22 | 0.23 | 0.14 | 0.25 | 0.3 | 0.27 | 0.37 | 0.34 |
| 6/21/2002 | 0.24 | 0.19 | 0.23 | 0.22 | 0.20 | 0.14 | 0.25 | 0.22 | 0.25 | 0.25 | 0.23 |
| 6/24/2002 | 0.14 | 0.14 | 0.14 | 0.23 | 0.16 | 0.11 | 0.17 | 0.16 | 0.16 | 0.21 | 0.17 |
| 7/2/2002 | 0.23 | 0.2 | 0.21 | 0.24 | 0.20 | 0.17 | 0.20 | 0.21 | 0.22 | 0.23 | 0.22 |
| 7/15/2002 | 0.26 | 0.22 | 0.24 | 0.23 | 0.24 | 0.20 | 0.24 | 0.23 | 0.26 | 0.26 | 0.25 |
| 7/18/2002 | 0.19 | 0.15 | 0.14 | 0.19 | 0.17 | 0.14 | 0.16 | 0.16 | 0.19 | 0.2 | 0.17 |
| 7/23/2002 | 0.26 | 0.22 | 0.26 | 0.16 | 0.24 | 0.21 | 0.24 | 0.26 | 0.26 | 0.25 | 0.26 |
| 7/26/2002 | 0.18 | 0.16 | 0.16 | 0.13 | 0.19 | 0.17 | 0.20 | 0.21 | 0.18 | 0.18 | 0.23 |
| 7/29/2002 | 0.244 | 0.226 | 0.24 | 0.17 | 0.23 | 0.25 | 0.26 | 0.25 | 0.22 | 0.21 | 0.25 |
| 8/6/2002 | 0.22 | 0.19 | 0.24 | 0.22 | 0.20 | 0.24 | 0.19 | 0.21 | 0.24 | 0.25 | 0.24 |
| 8/13/2002 | 0.2 | 0.21 | 0.18 | 0.23 | 0.21 | 0.18 | 0.21 | 0.22 | 0.25 | 0.26 | 0.25 |
| 8/16/2002 | 0.31 | 0.26 | 0.26 | 0.31 | 0.26 | 0.26 | 0.27 | 0.29 | 0.30 | 0.29 | 0.26 |
| 9/6/2002 | 0.21 | 0.18 | 0.20 | 0.20 | 0.21 | 0.24 | 0.20 | 0.21 | 0.30 | 0.25 | 0.24 |
| 9/17/2002 | 0.3 | 0.22 | 0.29 | 0.16 | 0.26 | 0.23 | 0.34 | 0.34 | 0.31 | 0.31 | 0.33 |
| 9/17/2002 | 0.3 | 0.22 | 0.29 | 0.16 | 0.26 | 0.23 | 0.34 | 0.34 | 0.31 | 0.31 | 0.33 |
| 9/18/2002 | 0.23 | 0.22 | 0.24 | 0.23 | 0.28 | 0.25 | 0.26 | 0.26 | 0.30 | 0.27 | 0.27 |
| 9/24/2002 | 0.23 | 0.17 | 0.15 | 0.17 | 0.14 | 0.14 | 0.14 | 0.16 | 0.14 | 0.18 | 0.14 |
| 9/25/2002 | 0.29 | 0.26 | 0.38 | 0.17 | 0.25 | 0.22 | 0.26 | 0.39 | 0.38 | 0.33 | 0.45 |
| 10/29/2002 | 0.21 | 0.23 | 0.25 | 0.26 | 0.22 | 0.19 | 0.25 | 0.24 | 0.25 | 0.22 | 0.24 |
| 11/4/2002 | 0.16 | 0.13 | 0.16 | 0.15 | 0.14 | 0.13 | 0.17 | 0.18 | | 0.19 | 0.31 |
| **Std Dev** | 0.054 | 0.042 | 0.063 | 0.044 | 0.044 | 0.048 | 0.053 | 0.078 | 0.060 | 0.049 | 0.071 |
| **MDL** | 0.135 | 0.106 | 0.157 | 0.112 | 0.110 | 0.119 | 0.132 | 0.195 | 0.150 | 0.123 | 0.178 |

**TABLE 2** MDL calculations of LFB analytes.
True Value for each analyte is 0.20 ug/mL

| Date | Ethalfluralin | Ethyl Parathion | Fenvalerate | Heptachlor | Heptachlor Epoxide | Malathion | Methoxychlor | Methyl Parathion | Metolachlor | Metribuzin | Prowl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/23/2002 | 0.18 | 0.15 | 0.31 | 0.14 | 0.20 | 0.34 | 0.32 | 0.29 | 0.26 | 0.28 | 0.24 |
| 6/3/2002 | 0.21 | 0.29 | 0.00 | 0.19 | 0.28 | 0.45 | 0.40 | 0.47 | 0.35 | 0.37 | 0.36 |
| 6/4/2002 | 0.18 | 0.16 | 0.28 | 0.11 | 0.19 | 0.28 | 0.25 | 0.26 | 0.24 | 0.22 | 0.22 |
| 6/18/2002 | 0.20 | 0.17 | 0.56 | 0.14 | 0.20 | 0.45 | 0.40 | 0.31 | 0.31 | 0.36 | 0.29 |
| 6/21/2002 | 0.20 | 0.22 | 0.47 | 0.17 | 0.20 | 0.33 | 0.30 | 0.26 | 0.26 | 0.38 | 0.26 |
| 6/24/2002 | 0.19 | 0.15 | 0.22 | 0.14 | 0.15 | 0.29 | 0.18 | 0.25 | 0.25 | 0.23 | 0.18 |
| 7/2/2002 | 0.22 | 0.20 | 0.33 | 0.14 | 0.19 | 0.30 | 0.25 | 0.26 | 0.24 | 0.24 | 0.22 |
| 7/15/2002 | 0.22 | 0.28 | 0.26 | 0.21 | 0.23 | 0.37 | 0.30 | 0.29 | 0.31 | 0.29 | 0.27 |
| 7/18/2002 | 0.21 | 0.25 | 0.25 | 0.10 | 0.16 | 0.25 | 0.15 | 0.25 | 0.21 | 0.26 | 0.25 |
| 7/23/2002 | 0.19 | 0.26 | 0.37 | 0.19 | 0.22 | 0.31 | 0.17 | 0.26 | 0.26 | 0.22 | 0.26 |
| 7/26/2002 | 0.08 | 0.18 | 0.19 | 0.10 | 0.16 | 0.18 | 0.29 | 0.13 | 0.17 | 0.13 | 0.12 |
| 7/29/2002 | 0.19 | 0.28 | 0.18 | 0.16 | 0.23 | 0.28 | 0.23 | 0.26 | 0.26 | 0.20 | 0.26 |
| 8/6/2002 | 0.18 | 0.26 | 0.26 | 0.17 | 0.20 | 0.34 | 0.26 | 0.26 | 0.26 | 0.29 | 0.25 |
| 8/13/2002 | 0.21 | 0.24 | 0.24 | 0.18 | 0.20 | 0.29 | 0.27 | 0.26 | 0.24 | 0.23 | 0.26 |
| 8/16/2002 | 0.22 | 0.24 | 0.26 | 0.24 | 0.26 | 0.29 | 0.30 | 0.29 | 0.33 | 0.31 | 0.31 |
| 9/6/2002 | 0.18 | 0.31 | 0.20 | 0.17 | 0.20 | 0.35 | 0.26 | 0.25 | 0.26 | 0.26 | 0.28 |
| 9/17/2002 | 0.17 | 0.36 | 0.30 | 0.14 | 0.22 | 0.36 | 0.34 | 0.32 | 0.15 | 0.23 | 0.28 |
| 9/17/2002 | 0.17 | 0.36 | 0.30 | 0.14 | 0.22 | 0.36 | 0.34 | 0.32 | 0.15 | 0.23 | 0.28 |
| 9/18/2002 | 0.22 | 0.29 | 0.26 | 0.18 | 0.70 | 0.33 | 0.26 | 0.26 | 0.26 | 0.23 | 0.26 |
| 9/24/2002 | 0.12 | 0.14 | 0.15 | 0.14 | 0.14 | 0.17 | 0.14 | 0.15 | 0.14 | 0.20 | 0.14 |
| 9/25/2002 | 0.18 | 0.37 | 0.48 | 0.36 | 0.24 | 0.39 | 0.26 | 0.38 | 0.26 | 0.32 | 0.31 |
| 10/29/2002 | 0.19 | 0.33 | 0.19 | 0.18 | 0.21 | 0.34 | 0.36 | 0.33 | 0.26 | 0.21 | 0.30 |
| 11/4/2002 | 0.09 | 0.17 | 0.18 | 0.08 | 0.14 | 0.22 | 0.17 | 0.19 | 0.17 | 0.09 | 0.14 |
| **Std Dev** | 0.038 | 0.072 | 0.119 | 0.057 | 0.110 | 0.071 | 0.074 | 0.069 | 0.056 | 0.070 | 0.058 |
| **MDL** | 0.096 | 0.181 | 0.298 | 0.142 | 0.275 | 0.177 | 0.185 | 0.174 | 0.142 | 0.174 | 0.146 |

**TABLE 2** MDL calculations of LFB analytes.
True Value for each analyte is 0.20 ug/mL

| Date | Simazine | Tilt | trans-Nonachlor | Triallate | Trifluralin |
|---|---|---|---|---|---|
| 5/23/2002 | 0.33 | 0.41 | 0.19 | 0.20 | 0.20 |
| 6/3/2002 | 0.53 | 0.53 | 0.28 | 0.26 | 0.26 |
| 6/4/2002 | 0.35 | 0.28 | 0.16 | 0.19 | 0.18 |
| 6/18/2002 | 0.37 | 0.71 | 0.15 | 0.22 | 0.20 |
| 6/21/2002 | 0.31 | 0.62 | 0.16 | 0.20 | 0.25 |
| 6/24/2002 | 0.29 | 0.27 | 0.12 | 0.21 | 0.17 |
| 7/2/2002 | 0.34 | 0.30 | 0.17 | 0.19 | 0.17 |
| 7/15/2002 | 0.30 | 0.41 | 0.20 | 0.26 | 0.24 |
| 7/18/2002 | 0.23 | 0.18 | 0.14 | 0.18 | 0.21 |
| 7/23/2002 | 0.26 | 0.45 | 0.21 | 0.22 | 0.17 |
| 7/26/2002 | 0.18 | 0.22 | 0.16 | 0.14 | 0.09 |
| 7/29/2002 | 0.24 | 0.19 | 0.23 | 0.22 | 0.20 |
| 8/6/2002 | 0.29 | 0.36 | 0.17 | 0.22 | 0.20 |
| 8/13/2002 | 0.25 | 0.37 | 0.18 | 0.23 | 0.22 |
| 8/16/2002 | 0.37 | 0.34 | 0.26 | 0.29 | 0.25 |
| 9/6/2002 | 0.26 | 0.39 | 0.17 | 0.21 | 0.19 |
| 9/17/2002 | 0.31 | 0.42 | 0.23 | 0.19 | 0.15 |
| 9/17/2002 | 0.31 | 0.42 | 0.23 | 0.19 | 0.15 |
| 9/18/2002 | 0.30 | 0.29 | 0.25 | 0.23 | 0.21 |
| 9/24/2002 | 0.20 | 0.14 | 0.21 | 0.14 | 0.23 |
| 9/25/2002 | 0.38 | 0.54 | 0.22 | 0.20 | 0.22 |
| 10/29/2002 | 0.44 | 0.41 | 0.19 | 0.26 | 0.23 |
| 11/4/2002 | 0.10 | | 0.13 | 0.13 | 0.10 |
| **Std Dev** | 0.089 | 0.142 | 0.042 | 0.039 | 0.044 |
| **MDL** | 0.222 | 0.357 | 0.107 | 0.098 | 0.111 |